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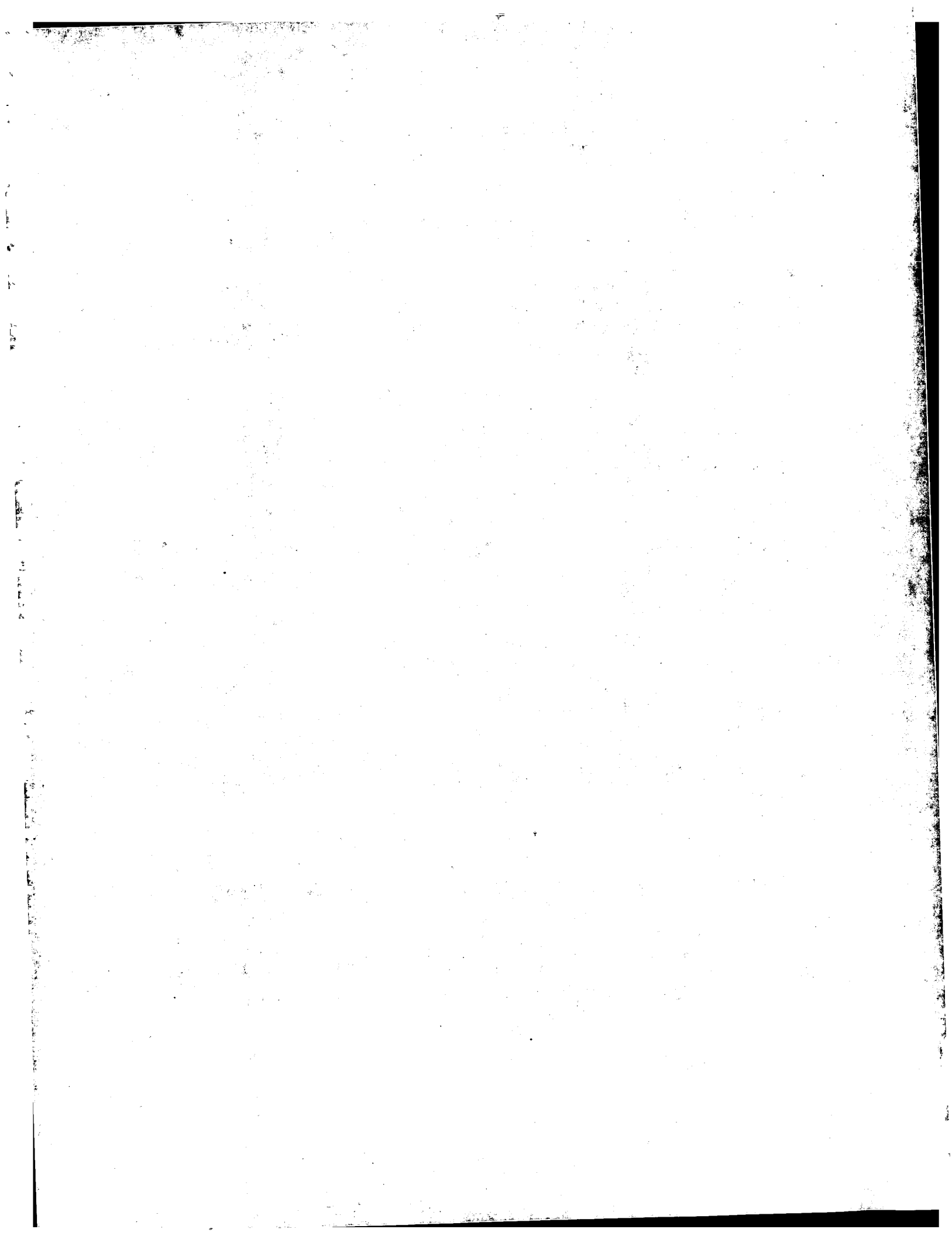
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(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 84107416.4

(51) Int. Cl.⁴: **C 08 L 27/16**
C 08 F 214/22

(22) Date of filing: 27.06.84

(30) Priority: 30.06.83 IT 2186583
23.05.84 IT 2105084

(43) Date of publication of application:
16.01.85 Bulletin 85/3

(84) Designated Contracting States:
BE CH DE FR GB LI NL SE

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(54) Fluoroelastomeric compositions based on a copolymer of vinylidene fluoride.

(57) Fluoroelastomeric compositions based on vinylidene fluoride, having a high adhesion to metals in the vulcanized state, and characterized in that they contain small amounts of chlorotrifluoroethylene which is present as a comonomer of an elastomeric copolymer of vinylidene fluoride in a mixture of fluoroelastomers or in one single fluoroelastomer.

TITLE MODIFIED
see front page

This invention relates to fluoroelastomeric compositions based on vinylidene fluoride, having a high adhesion to metals in the vulcanized state, and characterized in that they contain a minor amount of chlorotrifluoroethylene which is present as a comonomer of an elastomeric copolymer of vinylidene fluoride.

The fluoroelastomers with a high fluorine content have generally found a wider and wider utilization in the fields in which a high chemical stability and an excellent resistance to temperatures of 260°C for continuative use are required.

In a few of these utilizations, for example in the field of the sealing on rotary shafts accomplished by means of oil retaining rings, besides the characteristics which

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are typical of these elements, which are broadly described in literature (for example in Rubb. Ch. Tec. Vol. 55, page 5 908 (1982)), it is absolutely necessary that between the elastomer, constituting the sealing element of the gasket, and the metal insert, a perfect adhesion characterized by high adhesion coefficient values should be attained.

Therefore, there is the need for some manufactured 10 articles vulcanized from fluoroelastomers to reach a satisfactory vulcanization rate and processing safety, a high metal-to-rubber adhesion which, by remaining unaltered even at high temperatures, renders the vulcanized articles suitable for being used also under the most severe working 15 conditions.

The fluoroelastomeric compositions according to this invention can be prepared according to one of the two alternative methods described hereinafter.

According to the first method, an elastomeric copolymer 20 lymer of chlorotrifluoroethylene (5-70% by moles), of vinylidene fluoride (30-80% by moles) and optionally of hexafluoropropene (0-24% by moles) and/or tetrafluoroethylene (0-40% by moles), hereinafter referred to as copolymer A, is mixed with an elastomeric copolymer B based on vinyl- 25 idene fluoride (40-85% by moles), hexafluoropropene (15-25% by moles) and tetrafluoroethylene (0-32% by moles). The content of copolymer A in the total fluoroelastomeric composition ranges from 1.3 to 30% by weight and is such that the chlorotrifluoroethylene units are preferably in 30 the range of from 1 to 10% by weight, calculated on the

total.

Preferably, the content of $\text{CFCl}=\text{CF}_2$ units ranges from 5 1% to 2.7% by weight referred to the total polymeric mixture. For copolymer A, the preferred compositions, in moles, are : $\text{CH}_2=\text{CF}_2$ from 65% to 75%, $\text{CF}_2=\text{CFCl}$ from 10% to 35%, C_3F_6 from 0 to 30%, C_2F_4 from 0 to 25%. For elastomeric copolymer B of the type $\text{CH}_2=\text{CF}_2/\text{C}_3\text{F}_6$ the preferred compositions are : $\text{CH}_2=\text{CF}_2$ from 77% to 82% and C_3F_6 from 23 to 18%, while for the elastomeric copolymer of type $\text{CH}_2=\text{CF}_2/\text{C}_3\text{F}_6/\text{C}_2\text{F}_4$ the preferred compositions are : $\text{CH}_2=\text{CF}_2$ from 48 to 67%, C_3F_6 from 17 to 25%, C_2F_4 from 16 to 26%.

By means of the second method, the fluoroelastomeric composition according to the invention is prepared by employing an only fluoroelastomeric component, hereinafter referred to as fluoroelastomer C and consisting of a copolymer of vinylidene fluoride (54%-86% by moles), hexafluoropropene (13%-23%), chlorotrifluoroethylene (0.5% - 20 5%), tetrafluoroethylene (0-32%).

The best results are obtained with $\text{CF}_2=\text{CFCl}$ contents of from 0.8% to 2.5% by moles.

In both cases, if the chlorofluoroethylene content is below the minimum values indicated hereinabove, the vulcanizate does not exhibit satisfactory adhesion values, while 25 if the $\text{CF}_2=\text{CFCl}$ content is above the maximum limits indicated hereinabove for both cases, though obtaining high adhesion values, some drawbacks such as fouling of the molds and worsening of the vulcanized elastomer's properties 30 of chemical and thermal stability may occur.

The first method indicated herein offers the advantage of permitting to utilize, as basic fluoroelastomer, a vinylidene fluoride fluoroelastomer of the conventional type, imparting to it the desired value of adhesion to metals by admixture with a small amount of a fluoroelastomer having a high $\text{CF}_2=\text{CFCl}$ content.

Copolymers A according to the present invention are preferably prepared under the polymerization-in-emulsion conditions, in the presence of a radicalic starter. Suitable radicalic starters are the alkaline persulphates, perborates and percarbonates. It is also possible to employ a combination of peroxy starters with reducers, such as sulphites, bisulphites, metabisulphites, thiosulphates, phosphites or hyposulphites of alkaline metals or of ammonium, or copper (I) salts, Fe(II) salts, silver salts and other easily oxidizable metal salts. It is possible to use also organic radical starters and to operate in the presence of surfactants such as Na-laurylsulphate and ammonium perfluoro-octanoate. Of course, a surfactant may be used also when the copolymerization is carried out with an inorganic starter.

The presence of a chain transfer may be useful during the polymerization in emulsion.

The copolymer obtained by copolymerization in emulsion can be isolated from the latex according to conventional methods, for example coagulation with an electrolyte or by freezing, followed by filtration, washing and drying.

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The reaction providing the polymer may be also conducted in mass or in an organic liquid such as e.g. a chloro-
5 fluorohydrocarbon (Freon 113 or 114). It is preferable that the organic liquid present should not act as a chain transfer under the polymerization conditions; by consequence, Freon 114 is preferable to Freon 113.

During the copolymer preparation, the reaction mixture
10 ure is preferably heated in a pressure reactor, previously "washed" with an inert gas, to temperatures ranging from 45° to 135°C and pressures of from 4 to 40 kg/cm².

Copolymers A of chlorotrifluoroethylene according to the present invention exhibit, in most of cases, an inherent
15 viscosity ranging from 0.2 to 1.5 dl/g. The inherent viscosity of these polymers can be determined at 30°C in solvents such as, for example, methylethylketone, dimethylformamide, tetrahydrofuran, etc.

The Mooney viscosity of the copolymer ranges, in most
20 of cases, from 10 to 160, operating at 100°C with rotor I according to ASTM D 1646 standards.

The copolymers of type A according to this invention are generally preparable according to polymerization methods which are well known for the elastomers based on
25 vinylidene fluoride and broadly described in literature (US P 2,968,649, US P 3,051,677, US P 3,053,818, Encyclopedia of Chemical Technology, Kirk-Othmer, vol. 8, 3rd ed., pages 500-515 (1979)), taking care of introducing the desired amount of chlorotrifluoroethylene into the monomeric
30 mixture. Always operating according to what is described

hereinbefore, it is possible to obtain fluoroelastomers of group B by working in the absence of chlorotrifluoro-
5 ethylene.

Fluoroelastomer C according to the present invention is obtainable by means of polymerization methods known for the elastomers based on vinylidene fluoride and, in particular, it is possible to adopt a polymerization-in-emul-
10 sion process according to the operative techniques mentioned hereinabove for copolymer A. Fluoroelastomer C shall have, for the most widely used commercial products, an inherent viscosity between 0.2 and 1.5 dl/g. The Mooney viscosity will range, in most of cases, from 50 to
15 150, operating at 100°C with rotor L according to the standards mentioned hereinabove.

The vulcanizable fluoroelastomeric compositions according to the present invention, both those based on a mixture of copolymer A and of copolymer B (first method)
20 and those based on fluoroelastomer C only (second method), are preparable by using additives of a known type as vulcanizers, vulcanization accelerators, acid acceptors, etc.

Thus, a fluoroelastomeric composition conforming to this invention essentially comprises :

- 25 1) 100 parts by weight of a mixture of copolymer type A (from 1.3 to 30% by weight) and of copolymer type B (from 98.7 to 70% by weight), or 100 parts by weight of fluoroelastomer type C;
- 2) 1 to 40 parts by weight of an acceptor of inorganic
30 acids, which consists of at least a basic oxide of a

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divalent metal, such as magnesium oxide, calcium oxide, lead oxide;

- 5 3) 0.5 to 10 parts by weight of at least a basic hydroxide such as, for example calcium hydroxide, strontium hydroxide or barium hydroxide, and/or salts of weak acids of alkaline or alkaline-earth metals such as, e.g., calcium, strontium, barium, sodium, potassium
- 10 carbonates, benzoates and phosphates;
- 4) an aromatic polyhydroxyl cross-linking agent such as, for example, hydroquinone, hexafluoro-isopropylidene-bis-(4-hydroxy-benzene);
- 5) a vulcanization accelerator having the structure of a quaternary compound of nitrogen, of phosphorus, of
- 15 arsenic and of antimony in an amount ranging from 0.2 to 3 parts, as described in the following patents:
- | | |
|------------------------|--------------------------|
| GB 1,356,344 (Du Pont) | ammonium salts |
| US 3,876,654 (Du Pont) | phosphonium salts |
| 20 US 3,655,727 (EM) | ammonium salts |
| US 3,752,787 (Du Pont) | phosphoranes |
| UK 2,010,285 (ME) | amino-phosphonium salts. |

Compounds which are particularly useful for this invention are 1-tetrafluoroborate-1-benzyl-N,N',N"-hexamethyl-phosphoranetriamine, 1-chloro-1,1-diphenyl-1-benzyl-N-diethyl-phosphoranamine (prepared according to what is described in J.A.C.S. 84 5794 (1960)). Preparation of the mixes can be accomplished by operating as is described in the above-cited patents. The polymeric compositions according to the invention can be vulcanized also

25

30

with conventional vulcanizing systems. When it is desired to utilize vulcanizing systems based on organic peroxides, the fluoroelastomeric polymers according to the present invention can be properly modified by introducing into the polymeric chain small amounts of a brominated comonomer, such as $\text{BrCF}_2\text{-CF}_2\text{-O-CF=CF}_2$, in order to have in the fluoroelastomer from 0.1 to 1.5 % by weight of Br.

10 The preparation of a few copolymers employed for preparing the elastomeric compositions forming the object of the present invention is exemplified hereinafter.

Copolymer A.1

3.4 l of water were introduced into a 5-liter autoclave equipped with a mechanical stirrer. It was heated to 80°C whereafter, by means of a compressor, a mixture coming from a gasholder and having the following composition by moles was introduced into the autoclave:

vinylidene fluoride (VDF) 45.0%, hexafluoropropene (PFP) 25.0%, chlorotrifluoro-ethylene (CTFE) 30.0%, till reaching a pressure of 12 atm. gauge. 100 ml of an aqueous solution containing 10 g of ammonium persulphate were fed in. As the pressure decreased to 0.5 kg/cm² gauge, it was started again feeding the same gaseous composition contained in another gasholder and having the following composition : VDF = 75%, CTFE = 15%, PFP = 10%, in order to maintain a constant pressure of 12 kg/cm² gauge in the autoclave. After 80 minutes, 380 normal liters of monomers were consumed; stirring was stopped, the residual gases were discharged and the latex was collected, which

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was coagulated with aluminium sulphate and washed with water. The polymer, dried at 60°C, exhibited a Mooney viscosity of 74-ML1+4 (100°C) (ASTM.D 1545). Its composition in monomeric units was practically corresponding to the one of the mixture of the second gasholder.

Copolymer A.2

It was prepared according to the procedure described for elastomer 1, the mixture in the first gasholder having the following composition : VDF = 38%, PFP = 10%, CTFE = 52%, and the mixture in the second gasholder, the following composition : VDF = 66%, CTFE = 30%, PFP = 4%.

The polymer composition expressed in monomeric units was practically like that of the monomeric mixture coming from the second vessel. The Mooney viscosity was 76-ML1+4 (100°C).

Copolymer A.3

Always operating as is described hereinbefore, but with a composition in the first gasholder of : VDF = 50%, CTFE = 50%, and in the second gasholder of : VDF = 70%, CTFE = 30%, a copolymer was obtained, which had a composition practically like that of the mixture fed from the second gasholder, and a Mooney viscosity of 80-ML1+4 (10°C).

Copolymer A.4

Always operating as described hereinabove, but with a molar composition in the first gasholder of : VDF = 35%, CTFE = 15%, PFP = 40%, TFE = 10%, and in the second gasholder : VDF = 55%, CTFE = 15%, PFP = 15%, TFE = 15%, a copolymer was obtained, whose composition was practical-

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ly like that of the mixture fed / ^{from} the second gasholder.
The Mooney viscosity was 82-ML1+4 (100°C).

5 Elastomer B.1

It was prepared by operating as is described for copolymer A.1 with a gaseous feeding mixture of VDF + PFP in gasholder 1 and in gasholder 2 in a VDF/PFP molar ratio of 1 and 4, respectively.

10 An elastomer was obtained having a composition of about 20% by moles of PFP and 80% by moles of VDF, and a Mooney viscosity of 85-ML1+4 (100°C).

Elastomer B.2

This terpolymer based on VDF + PFP + TFE was prepared
15 by operating in the same manner as for copolymer B.1 feeding a gaseous composition VDE/PFP/TFE from the second gasholder in a molar ratio of 3/1/1 and ^{from} the first gasholder of 2/1/1.

The obtained polymer had the following molar composition : VDF = 60%, PFP = 20%, TFE = 20%, and a Mooney
20 viscosity = 88-PL1+4 (100°C).

Examples 1-8 (Table I)

The examples of Table I as well as the successive ones are given in order to illustrate the characteristics
25 of the vulcanizates obtained from the mixtures of elastomeric copolymers according to the invention. All the indicated amounts are amounts by weight, unless otherwise specified.

In the tables there are indicated the formulations
30 employed, in which there are contained the fluoroelastom-

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ers prepared as described hereinabove, namely : composition 1 comprises a mixture of 6.7 parts by weight of copolymer A.1 and 93.3 parts by weight of elastomer B.1; composition 2 comprises a mixture of 13.4 parts of copolymer A.1 and 86.6 parts of elastomer B.1; composition 3 comprises 26.8% b.wght. of A.1 and 73.2% by weight of elastomer B.1.; composition 4 is composed of a mixture of copolymer A.2 (6.7% by weight) and of elastomer B.1 (93.3% by weight); composition 5 consists of a mixture of copolymer A.2 (26.8% by weight) and of elastomer B.1 (73.2% by weight); composition 6 consists of a mixture of copolymer A.3 (6.7% by weight) and of elastomer B.1 (93.3% by weight), while composition 7 comprises a mixture of copolymer A.3 (13.4% by weight) and of elastomer B.1 (86.6% by weight).

Accelerator 1 is 1-tetrafluoroborate-1-benzyl-N,N',N''-hexamethyl-phosphoranetriamine.

To evaluate the adhesion between vulcanized elastomeric composition and metal, standard ASTM D 816, method B - "Adhesion strength in shear" was utilized, since the methods based on peeling or stripping measures are also bound to the rubber's tearing resistance.

Specimens in the form of sandwiches, as schemetically shown in figure 1 (wherein: M = metal, G = rubber, A = adhesive), were prepared. The small metal plates (carbon steel UNI Fe 37 A, dimensions: 80x25x2 mm) were degreased in a vapour bath of Alkofrene 113 (1.1.2-trichloro-trifluoroethane) and sandblasted with corundum

(granulometry = 0.01 mm) in the adhesion areas, then degreased once again. The adhesive was applied by spraying onto the portion intended for adhesion.

As an adhesive, Chemosil 511, a trademark of Henkel, was used.

The adhesion between the plates treated with the adhesive and the elastomer occurred during the vulcanization-in-press step. The overlapping surface was of about 625 mm² (rubber thickness = 3.8 mm).

Molding conditions : $P = 60-70 \text{ kg/cm}^2$

$T = 170 \pm 2 \text{ }^\circ\text{C}.$

The time was a function of the accelerator concentration and of the CTFE content.

The specimens so prepared were subjected to tensile strength at a speed of 50 mm/min. The adhesion resistance was evaluated after vulcanization in press, after post-vulcanization in an oven at 250°C and after post-vulcanization at 250°C followed by treatment in boiling water.

In the cases in which a breaking of the joint and failure of the bondage resp. occurred through the rubber, the adhesion resistance was considered to be higher than the measured value.

All the mechanical tests are referred to a temperature of 23°C.

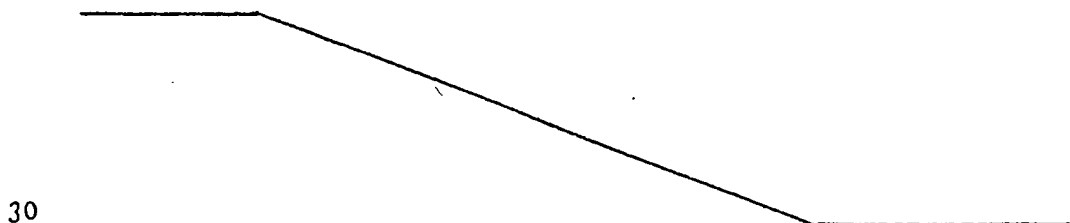


TABLE I

EXAMPLES	1	2	3	4	5	6
Elastomer B.1 p.b.wght.	100	100				
Composition 1 "			100			
Composition 2 "				100		
Composition 3 "					100	
Composition 4 "						100
Composition 5 "						
Composition 6	1.8	1.8	1.8	1.8	1.8	1.8
Composition 7	0.350	0.350	0.350	0.350	0.350	0.350
Bisphenol AF						
Accelerator 1	5	5	5	5	5	5
Maglite DE (MgO)	5	5	5	5	5	5
Ca(OH) ₂						
Carbon black MT	25	25	25	25	25	25
<u>Thermomechanical characteristics</u>						
O.D.R. at 175°C (1)						
Minimum torque (lb.in.)	12	12	13	13	12	13
Ts 2 (min.)	2.7	3.1	3.4	3.5	3.2	3.8
t'c (min.)	4.5	5.1	5.4	5.9	5.5	5.8
Maximum torque (lb.in.) 12 minut.	102	101	98	85	96	82
<u>Vulcanizate</u>						
Adhesion (kg/cm ²) (2)						
After vulcanization in press at 175°C x 8 minutes	7	27	46	53	47	51
After post-vulcanization in oven at 250°C x 16 hours	15	22	25	46	26	38

(1) According to ASTM D 2084

(2) According to ASTM D 816 - method B

TABLE I (second part)

	Examples		7	8
	p.b.wght.			
5	Elastomer B.1			
	Composition 1			
	Composition 2			
	Composition 3			
	Composition 4			
	Composition 5			
	Composition 6	"	100	
10	Composition 7	"		100
	Bisphenol AF	"	1,8	1,8
	Aceclerator 1	"	0.350	0.350
	Maglite DE (MgO)	"	5	5
	Ca(OH) ₂	"	5	5
15	Carbon ² black MT	"	25	25
	<u>Thermomechanical characteristics</u>			
	O.D.R. at 175°C (1)			
	Minimum torque (lb.in.)		13	12
20	Ts 2 (min.)		3,3	3,6
	t' (min.)		5,4	5,9
	Maximum ^c torque (lb.in.) 12 minutes		92	84
25	<u>Vulcanizate</u>			
	Adhesion (kg/cm ²) (2)			
	After vulcanization in press at 175°C x 8 minutes		48	55
	After post-vulcanization in oven at 250°C x 16 hours		27	44
30				

(1) According to ASTM D 2084

(2) According to ASTM D 816, method B

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Examples 9-12 (Table 2)

Composition 8 comprised 6.7% by weight of copolymer A.4 and 93.3% of elastomer B.2.

5 Composition 9 comprised 13.4% by weight of copolymer A.4 and 93.3% of elastomer B.2.

Composition 10 consisted of 26.8 parts by weight of copolymer A.4 and of 73.2 parts by weight of elastomer B.2.

Accelerator 2 was 1-chloro-1,1-diphenyl-1-benzyl-N-
10 -diethylphosphoramine.

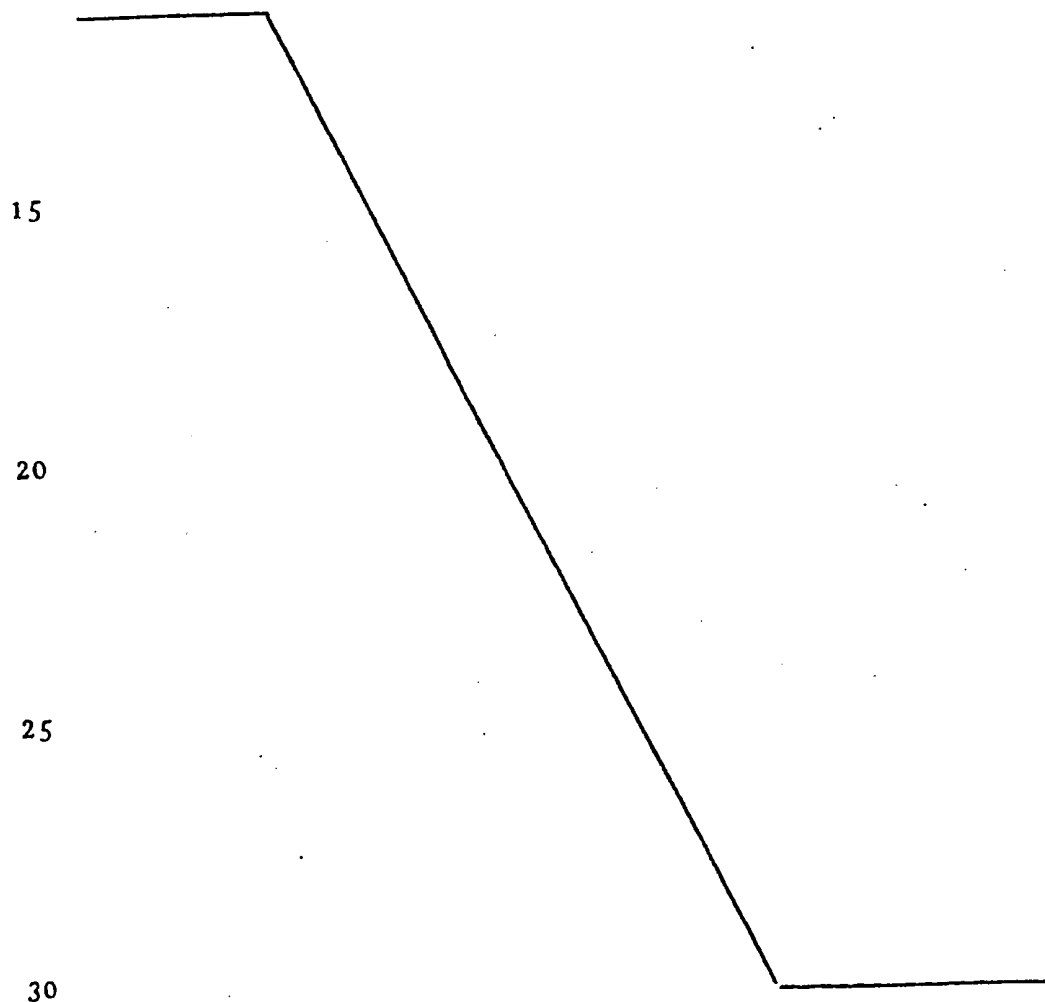


TABLE 2

Examples		9	10	11	12
5	Elastomer B.2	100			
	Composition		100		
	Composition			100	
	Composition				100
	Composition				
10	Bisphenol AF	1,6	1,6	1,6	1,6
	Accelerator 2	0,550	0,550	0,550	0,550
	Maglite DE	5	5	5	5
	Ca(OH) ₂	5	5	5	5
	Carbon ² black MT	25	25	25	25
<u>Thermomechanical characteristics</u>					
15	O.D.R. at 175°C (1)				
	Minimum torque (lb.in.)	22	22	23	25
	ts (2) (min.)	3,1	3,4	3,6	3,8
	t' (50)	4,0	4,4	4,6	4,9
	Maximum torque (lb.in.)	132	121	115	108
20	<u>Vulcanizate</u>				
	Adhesion (kg/cm ²) (2)				
	After vulcanization in press at 175°C x 8 minutes	6	31	36	43
25	After post-vulcanization in oven at 250°C x 16 hours	13	21	25	36
30					

(1) See note in Table I

(2) See note in Table I

The preparation of elastomers type C will be now described.

5 Elastomer C.1

3.4 l of water were charged into a 5-liter autoclave equipped with a mechanical stirrer. Hexafluoropropene was introduced by means of autogenous pressure in such way as to cause the pressure inside the autoclave to reach 5 atm.

10 Now it was heated by means of a compressor, and a mixture coming from a gasholder and having the following composition by moles was introduced : vinylidene fluoride (VDF) = 79.4%, hexafluoropropene (PFP) = 19.6%, chloro-trifluoro-ethylene (CTFE) = 1%, till reaching a pressure
15 of 12 kg/cm² gauge. 100 ml of an aqueous solution containing 10 g of ammonium persulphate were fed. As the pressure decreased to 0.5 kg/cm² gauge, feeding of the same gaseous composition contained in the gasholder was started again in order to maintain a constant pressure of 12 kg/
20 cm² gauge in the autoclave. After 80 minutes, 380 normal liters of monomer were consumed; stirring was stopped, the residual gases were discharged and the latex was collected, which was coagulated with aluminium sulphate and washed with water. The polymer, dried at 60°C, exhibited
25 a Mooney viscosity of 76-ML1+4 (100°C) (ASTM D 1646). Its composition in monomeric units was practically corresponding to the one of the mixture in the gasholder.

Elastomer C.2

It was prepared according to the procedure described
30 for elastomer C.1, the mixture in the gasholder having

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the following composition : VDF = 79%, PFP = 19%,
CTFE = 2%.

5 The polymer composition expressed in monomeric units
was the same of the fed monomeric mixture.

Mooney viscosity was 74-ML1+4 (100°C).

Elastomer C.3

Always operating as is described hereinbefore, but
10 with a monomer composition corresponding to VDF = 79.3%,
PFP = 19.2%, CTFE = 1.5% and an ammonium persulphate
content of 8 g, a copolymer was obtained having a compos-
ition practically equal to the one of the fed mixture and
a Mooney viscosity of 78-ML1+4 (100°C).

15 Elastomer C.4

It was obtained by operating analogously with what
is described for elastomer C.3, but with the following
composition of the fed mixture: VDF = 77.5%, PFP = 19%,
CTFE = 3.5%. Polymerization was conducted at 15 atm.

20 Mooney viscosity = 72-ML1+4 (100°C).

Elastomer C.5

It was obtained in like manner as is described
hereinbefore.

Composition : VDF = 80%, PFP = 15%, CTFE = 5%.

25 Mooney viscosity = 70-ML1+4 (100°C).

Elastomer 6 (comparative)

It was prepared by operating as for elastomer C.1,
with a gaseous feeding mixture having a VDF/PFP molar
ratio = 4 and in the absence of CTFE.

30 The resulting polymer had this composition:

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VDF = 80%, PFP = 20%, and a Mooney viscosity = 78-ML1+4 (100°C).

5 Examples 13 - 24 (Table 3) and 25 - 30 (Table 4)

These examples as well as the successive ones are given in order to illustrate the characteristics of the vulcanizates obtained from elastomers type C according to the invention. All the indicated amounts are by weight, unless otherwise specified.

In the tables there are indicated the formulations employed, in which there are contained the fluoroelastomers prepared as described hereinbefore, namely elastomers C.1, C.2, C.3, C.4 and C.5 according to the invention, and elastomer 6 according to the art, by way of comparison.

15 The adhesion between vulcanized elastomer and metal was evaluated according to the method described for examples 1 - 8.

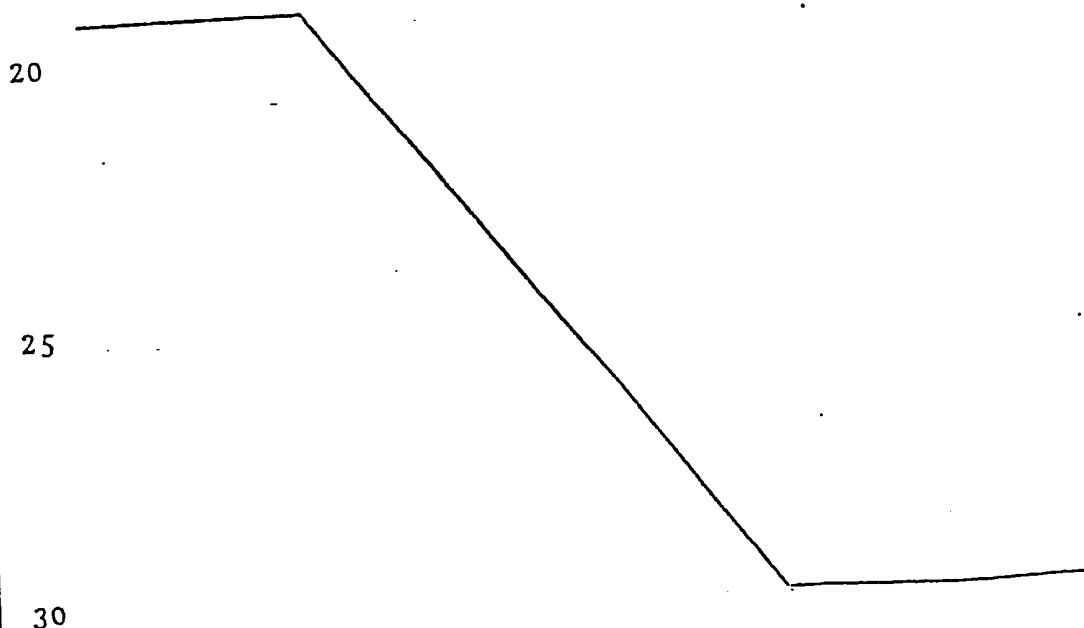


TABLE 3

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Example	1	2	3	4	5	6
Elastomer C.1 by weight	100	100	100	100	-	-
Elastomer C.2 " "	-	-	-	-	100	100
Elastomer 6 " "	-	-	-	-	-	-
Maglite DE (MgO) " "	5	5	5	5	5	5
Ca(OH) ₂ " "	5	5	5	5	5	5
Carbon ² black MT " "	25	25	25	25	25	25
Bisphenol AF " "	1,8	1,8	1,8	1,8	1,8	1,8
Accelerator 1 (as in examples 1-8) " "	0,250	0,300	0,350	0,450	0,250	0,300
<u>Thermomechanical characteristics</u>						
O.D.R. at 175°C (1)						
Minimum torque in.lb.	12	10	11	13	14	12
T _s (2) minutes	4.2	3,7	3,4	2,9	3,5	3,0
T _c (50) minutes	9.7	6,2	6,5	3,4	7,0	5,7
Maximum torque in.lb	68	83	87	91	70	86
Mooney viscosity MS at 121°C (2)						
- minimum value:	43	42	40	38	44	47
- minutes for an increase by 10 points (t10) :	50	48	44	40	45	42
<u>Vulcanization</u>						
in press 170°C x 10 minutes						
in oven 250°C x 16 hours						
Modulus at 100% elong.kg/cm ² (3)	42	43	48	55	43	46
Tensile strength " (3)	155	162	161	158	170	175
Elongation at break % (3)	190	210	209	195	195	205
Hardness, IRHD (4)	67	67	69	71	68	70
Compression set						
O-rings (Ø 25.4x3.53 mm) (5)						
200°C x 70 hours	19	20	22	23	18	20
<u>Vulcanizate</u>						
Adhesion (6) kg/cm ² :						
After vulcanization in press						
at 175°C x 8 minutes	50	45	39	29	> 50	> 55
After post-vulcanization in oven						
at 250°C x 16 hours	41	40	27	24	> 53	> 57
After thermal ageing						
at 250°C x 16 hours and						
aqueous treatment at 100°C						
x 48 hours	32	31	30	20	> 47	> 53

- 1) according to ASTM D 2084
- 2) according to ASTM D 1646
- 3) according to ASTM D 412 on 2 mm thickness

- 4) according to ASTM D 1415 on 6 mm thick specimens
- 5) according to ASTM D 395 method B
- 6) according to ASTM D 816 method B

TABLE 3 (continuation)

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Example	7	8	9	10	11	12
Elastomer C.1 b.weight	-	-	-	-	-	-
Elastomer C.2 " "	100	100	-	-	-	-
Elastomer 6 " "	-	-	100	100	100	100
Maglite DE (MgO) " "	5	5	5	5	5	5
Ca(OH) ₂ " "	5	5	5	5	5	5
Carbon ² black MT " "	25	25	25	25	25	25
Bisphenol AF " "	1,8	1,8	1,8	1,8	1,8	1,8
Accelerator 1 (as in examples 1-8) " "	0,350	0,450	0,250	0,300	0,350	0,450
<u>Thermomechanical characteristics</u>						
O.D.R. at 175°C (1)						
Minimum torque in.lb	12	8	9	9	9	10
T _s (2) minutes	2,7	2,4	4,6	3,2	3,1	2,2
T' _c (50) minutes	4,9	4,2	8,9	5,4	4,9	3,2
Maximum torque in.lb	88	84	88	88	94	100
<u>Mooney viscosity</u> MS at 121°C (2)						
- minimum value :	40	37	55	52	50	46
minutes for an increase by 10 points (t10):	38	36	60	58	55	45
<u>Vulcanization</u>						
in press 170°C x 10 minutes						
in oven 250°C x 16 hours						
Modulus at 100% elong. kg/cm ² (3)	50	55	44	48	58	67
Tensile strength " (3)	171	165	163	157	147	166
Elongation at break % (3)	200	195	193	179	163	178
Hardness, IRHD (4)	70	71	71	72	74	75
Compression set						
O-rings (Ø 25.4x3.53 mm) (5)						
200°C x 70 hours	21	21	17	19	20	21
<u>Vulcanizate :</u>						
Adhesion (6) kg/cm ² :						
After vulcanization in press						
at 175°C x 8 minutes	> 70	> 49	24	11	10	6
After post-vulcanization in oven						
at 250°C x 16 hours	> 43	> 41	25	23	27	15
After thermal ageing						
at 250°C x 16 hours and						
aqueous treatment at 100°C						
x 40 hours	> 36	> 40	21	19	23	16

- | | |
|--|---|
| 1) according to ASTM D 2084 | 4) according to ASTM D 1415 on 6-mm-thick specimens |
| 2) according to ASTM D 1646 | |
| 3) according to ASTM D 412 on 2 mm thickness | 5) according to ASTM D 395 method B |
| | 6) according to ASTM D 816 method B |

TABLE 4

Example	13	14	15	16	17	18
Elastomer C.3						
Elastomer C.4						
Elastomer C.5						
Maglite DE (MgO)						
Ca(OH) ₂						
Carbon ² black MT						
Bisphenol AF						
Accelerator 1 (as in examples 1-8)						
<u>Thermomechanical characteristics</u>						
O.D.R. at 175°C (1)						
Minimum torque in/lb						
T _s (2) minutes						
T _c (50) minutes						
Maximum torque in.lb						
Mooney viscosity MS at 121°C (2)						
- minimum value:						
- minutes for an increase by 10 points (t10):						
<u>Vulcanization</u>						
in press 170°C x 10 minutes						
in oven 250°C x 16 hours						
Modulus at 100% elong. kg/cm ² (3)						
Tensile strength " (3)						
Elongation at break % (3)						
Hardness, IRHD (4)						
Compression set						
O-rings (Ø 25.4 x 3.53 mm) (5)						
200°C x 70 hours						
<u>Vulcanizate:</u>						
Adhesion (6) kg/cm ² :						
After vulcanization in press						
at 175°C x 8 minutes						
After post-vulcanization in oven						
at 250°C x 16 hours						
After thermal ageing						
at 250°C x 16 hours and						
aqueous treatment at 100°C						
x 48 hours						

1) according to ASTM D 2084

4) acc.to ASTM D 1415 on 6-mm thick spec:

2) according to ASTM D 1646

5) acc.to ASTM D 395 method B

3) according to ASTM D 412 on 2-mm thickness

6) according to ASTM D 816 method B

(*) vulcanization in press at 170°C x 15 minutes.

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EXAMPLES 31 to 36

These examples evidence how elastomers type C.1[^] prepared according to the present invention permit to obtain a good adhesion also when the fluorine content of the copolymer is high, up to 69% by weight approximately.

As is known, the stability of the fluoroelastomers based on vinylidene fluoride to the organic solvents is highly depending on the fluorine content (L.D. Albin, Rubb. Chem. Technol. 55, page 903 (1982)). The values of adhesion to metal, of chemical stability and of behaviour to low temperatures, evaluating the last value as Tg or glass transition temperature (method DSC with $dT/dt = 10^{\circ}\text{C}/$ min. and brittle point (ASTM D 746) were compared between polymers according to the present invention and polymers according to the art having an equal fluorine content (about 69% by weight), a different composition, and always having 1.5% by moles of CTFE.

Elastomer C.7 was prepared in the same manner as elastomer C.1 and exhibited the following composition: ($T_g = -4.0^{\circ}\text{C}$)

	$\text{C}_2\text{H}_2\text{F}_2$	52.5 %
	C_3F_6	22.0 %
	C_2F_4	24.0 %
25	C_2ClF_3	1.5 %

Elastomer C.8 was prepared according to what is described in US patent 4,032,699 and had the following composition : ($T_g = -4.5^{\circ}\text{C}$)

	$\text{C}_2\text{H}_2\text{F}_2$	37.5 %
30	C_3F_6	61.0 %

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 C_2ClF_3 1.5 %

Reference elastomer 9 was prepared as elastomer C.7

5 without C_2ClF_3 ; the composition was the following :
($T_g = -5.0^\circ C$)

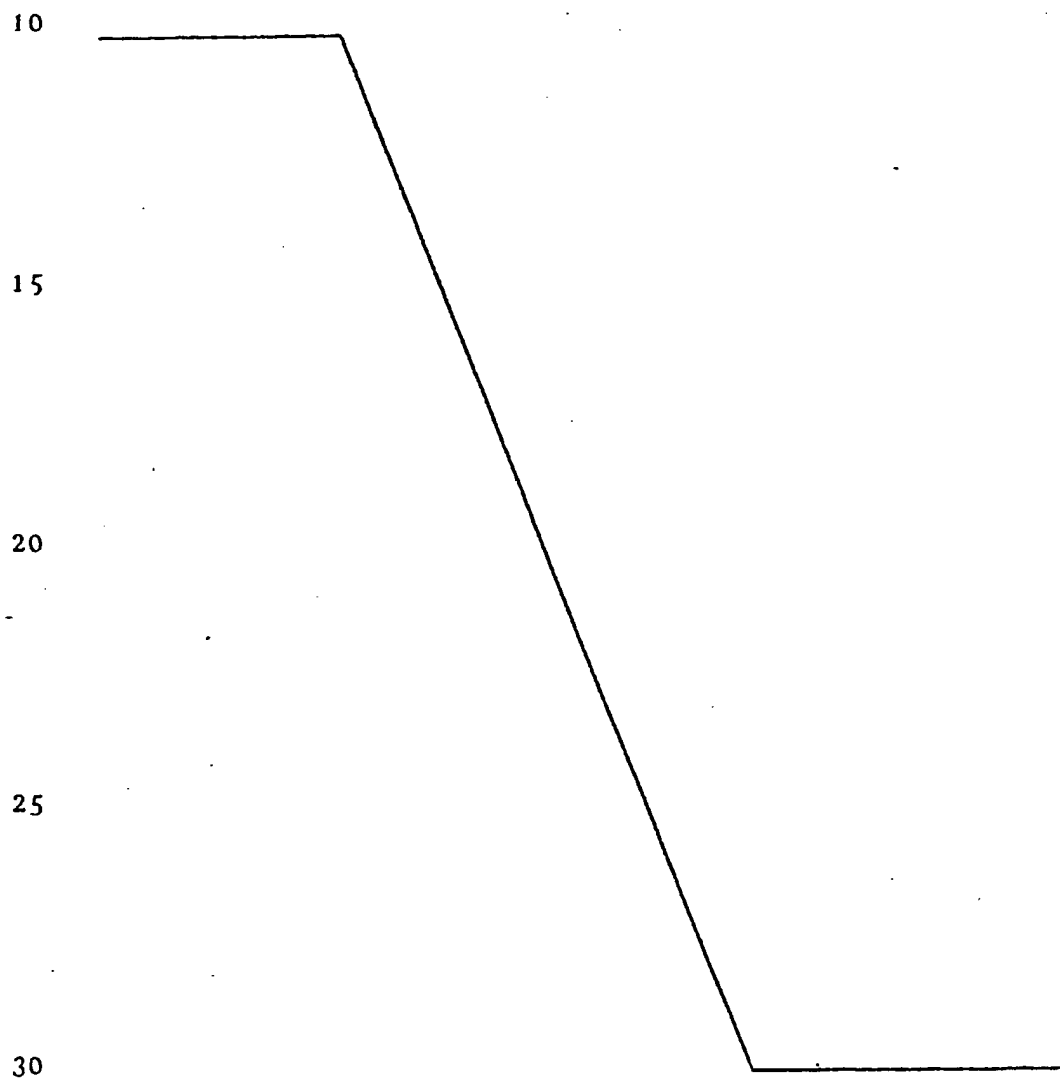
 $C_2H_2F_2$ 53.3 % C_3F_6 22.33 % C_2F_4 24.37 %

TABLE 5

Example	19	20	21	22	23	24
Elastomer C.7 b.weight	100	100	-	-	-	-
Elastomer C.8 " "	-	-	100	100	-	-
Elastomer 9 " "	-	-	-	-	100	100
Maglite DE " "	3	3	3	3	3	3
Ca(OH) ₂ " "	6	6	6	6	6	6
Carbon ² black MT " "	30	30	30	30	30	30
Bisphenol AF " "	2,7	2,7	2,7	2,7	2,7	2,7
Accelerator 1 (as in examples 1-8) " "	0,9	1,1	0,9	1,1	0,9	1,1
<u>Vulcanization</u>						
in press 170°C x 10 minutes						
in oven 250°C x 16 hours						
Modulus at 100% elong. kg/cm ² (3)	58	58	60	61	55	55
Tensile strength " (3)	135	140	120	130	155	160
Elongation at break % (3)	220	225	246	245	235	230
Hardness, IRHD (4)	75	77	83	77	74	75
Compression set,						
O-rings (Ø 25.4x 3.53 mm) (4)						
200°C x 70 hours	25	27	26	28	36	38
Brittle point (8) °C	-37	-37	-7	7	-38	-38
Chemical stability (7)						
Toluene 25°C x 70 hours	5.1	4,8	4,8	4,2	4,5	4,3
Stauffer blend 7700						
200°C x 70 hours	11,5	11	10,9	10,2	10,1	9,8
Adhesion (6) kg/cm ²						
After vulcanization in press						
at 175°C x 8 minutes	> 51	> 46	23	25	21	24
After post-vulcanization in oven						
at 250°C x 16 hours	> 46	> 42	21	23	22	23
After thermal ageing						
at 250°C x 16 hours and						
aqueous treatment at 100°C	> 40	> 39	15	14	14	16
x 48 hours						

3) according to ASTM D 412 - on 2 mm specimens

4) according to ASTM D 1415 - on 6 mm thick specimens

5) according to ASTM D 395 - method B

6) according to ASTM D 816 - method B

7) according to ASTM D 471 - i numbers indicate the % by weight of swelling

8) according to ASTM D 746



C l a i m s

- 1.- Vulcanizable fluoroelastomeric compositions, having a high adhesion to metals in the vulcanized state, comprising an elastomeric copolymer containing vinylidene fluoride and chlorotrifluoroethylene.
- 2.- A composition according to claim 1, comprising a mixture of fluoroelastomers consisting of 1.3 to 30 parts by weight of a copolymer A containing from 5 to 70 % by mole of $\text{CF}_2=\text{CFCl}$, from 30 to 80 % by mole of $\text{CH}_2=\text{CF}_2$, from 0 to 24 % by mole of C_3F_6 , and from 0 to 40 % by mole of C_2F_4 , and of 98.7 to 70 parts by weight of a copolymer B containing from 40 to 85 % by mole of $\text{CH}_2=\text{CF}_2$, from 15 to 25 % by mole of C_3F_6 , from 0 to 32 % by mole of C_2F_4 .
- 3.- A composition according to claim 2, in which the content of $\text{CF}_2=\text{CFCl}$ in the total polymeric mixture ranges from 1 to 2.7 % by weight.
- 4.- A composition according to one of claims 2 or 3 in which copolymer A consists of 65 to 75 % by mole of $\text{CH}_2=\text{CF}_2$, 10 to 35 % by mole of $\text{CF}_2=\text{CFCl}$, 0 to 30 % by mole of C_3F_6 and 0 to 25 % by mole of C_2F_4 .
- 5.- A composition according to one of claims 2 to 4 in which copolymer B of the type $\text{CH}_2=\text{CF}_2/\text{C}_3\text{F}_6$ consists of 77 to 82 % by mole of $\text{CH}_2=\text{CF}_2$ and 23 to 18 % by mole of C_3F_6 .
- 6.- A composition according to one of claims 2 to 4 in which copolymer B consists of 48 to 67 % by mole of $\text{CH}_2=\text{CF}_2$, 17 to 25 % by mole of C_3F_6 , and of 16 to 26 % by mole of C_2F_4 .
- 7.- A composition according to claim 1, comprising a fluoroelastomer C consisting of 54 to 86 % by mole of $\text{CH}_2=\text{CF}_2$, 13 to 23 % by mole of C_3F_6 , 0.5 to 5 % by mole of $\text{CF}_2=\text{CFCl}$ and of 0 to 32 % by mole of C_2F_4 .
- 8.- A composition according to claim 7 in which the content of $\text{CF}_2=\text{CFCl}$ in the fluoroelastomer ranges from 0.8 to 2.5 % by mole.
- 9.- Vulcanized articles prepared from fluoroelastomeric compositions according to any of the preceding claims 1 to 8.

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T 3 2 0 9 +

T. 3 2 8 7

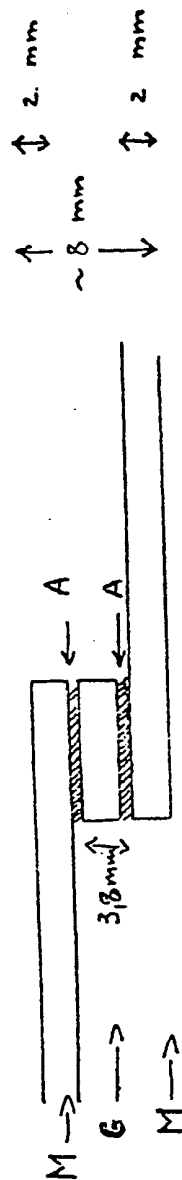


FIGURE I



European Patent
Office

EUROPEAN SEARCH REPORT

0131203
Application number

EP 84 10 7416

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. *)
X,D	US-A-4 032 699 (A. WEST) * Claim 1; column 6, table 1 * -----	1,7-9	C 08 L 27/16 C 08 F 214/22
			TECHNICAL FIELDS SEARCHED (Int. Cl. *)
			C 08 F C 08 L
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 12-10-1984	Examiner HOFFMANN K.W.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			
T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

